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Ceramic Coatings for Corrosion Environments

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This paper presents some of the recent experience with ceramic heat exchanger technology in the corrosive environment of the aluminum remelt industry. It also addresses the use of coatings technology to improve the resistance of ceramics to the most severe environments.

Introduction

Heat recovery in industrial processes for the refining of aluminum and copper, for the melting of fiber glass, container glass, and flat glass, for the heating of steel ingots, and for waste incineration can be carried out efficiently with ceramic heat exchangers. Metallic heat exchangers which perform adequately in processes with clean stack gases are limited to temperatures of about 700°C in the severely corrosive environments of the industrial processes. On the other hand, heat exchangers utilizing silicon carbide heating elements allow operation at temperatures in excess of 1200°C because of the superior resistance of the ceramic material to the corrosive stack gases in these industrial processes.

Ceramic Heat Exchanger Technology

The heat recovery system developed by Solar Turbines Incorporated, partially under the sponsorship of the Gas Research Institute of Chicago, uses high quality structural silicon carbide tubular components for the heat transfer surfaces. The tubes are configured into the self-contained modules schematically represented in Fig. 1.

These modules are fabricated using 12 to 16 silicon carbide ceramic tubes (with one end closed) to form bayonet-style heat recovery modules. The ceramic tubes can vary in size from 4.45 to 7.62 cm (1.75 to 3 in.) in diameter and 1.52 to 1.82 m (5 to 6 ft) in length as required by the application. A sixteen-tube module used in the current production recuperator is shown in Fig. 2. Energy from the process exhaust gases is transferred to clean combustion air flowing through the ceramic recuperator tubes which extend into the process exhaust gas stream.

Modules can be arranged one behind another to form a single-pass recuperator. Figure 3 shows how two of these multimodule components can be configured into a two-pass recuperator.

A critical element in the recuperator design is the ceramic-to-metal joint which bonds each ceramic tube permanently to the metal sleeve. The bond creates a leak-free condition which can be maintained for pressures up to 1 MPa (150 psi).

Figure 4 shows a view of Solar's ceramic recuperator which is currently operating in a field test on top of an aluminum remelt furnace at TIMCO Incorporated, in Fontana, California. The heat exchanger which started operation on April 1, 1985, has accumulated over 13 000 hours of continuous operating time except for minor shut-downs for maintenance.

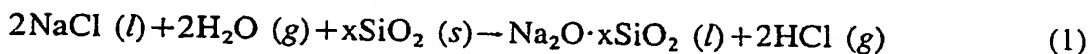
The field test furnace is a reverberatory-aluminum remelt furnace sized to hold 81 450 kg (180 000 lbs) of molten metal. Not one of the 384 silicon carbide ceramic tubes (nearly 610 m [2000 ft]) contained in this recuperator has failed. Maximum gas side inlet temperature was 1010 °C and a maximum air preheat of 600 °C was achieved. The overall thermal effectiveness was estimated to be 55 %. More detailed accounts of this recuperator technology and the results of the field test have been given elsewhere.¹⁻³

Corrosion Environment

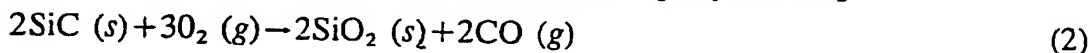
The recuperator field test at the TIMCO remelt facility was performed in a moderately corrosive environment. The recuperator utilizes stack gases containing alkali chloride vapors from the fluxing agents used in the aluminum remelting process. A noticeable performance degradation (reduced thermal effectiveness) was observed as a result of salt accumulations on the heat transfer surfaces after about 4500 hours of recuperator operation. Removal of the salt resulted in a return of the performance to prefouling levels. No visible signs of corrosion could be detected, and tube wall recession rates were on the order of 0.013 cm for 0.478-cm-thick walls, i.e., within the dimensional tolerance of the tubes. Long tube life in excess of 5 years appears to be within current expectations for this application.

The stack gas environment can be substantially more corrosive. In a concurrent study, potential recuperator tubular ceramic materials (SiC) were exposed to the exhaust gases of an aluminum remelt process which utilizes fluorine containing fluxes. When fluorine compounds are used in the fluxing agents of an aluminum remelt process, the corrosive potential of the process stack gases becomes more severe than that of the above described TIMCO process.

The synergism between the alkali (Na, K) and the fluorine compounds of the stack gases results in rapid degradation of the normally protective SiO₂ surface layer on the SiC heat transfer surfaces. Chemical analysis of the surface corrosion deposits (Table I) revealed high concentrations of Na and K suggesting that glass forming reactions may be involved in the tube degradation process. These glass forming reactions presumably involve condensed alkali halides in the gas phase and the surface SiO₂ layer, e.g.,

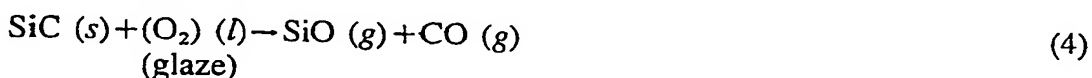
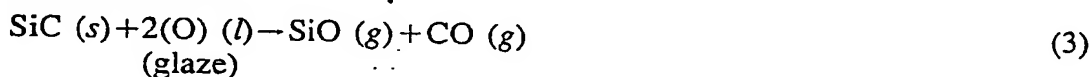


The fluxing of the SiO₂ by alkali halide salt condensates on reactive surface glazes exposes a virgin SiC surface which reoxidizes rapidly to SiO₂

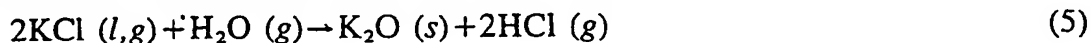


This type of "passive" oxidation is the ruling mode at fairly high oxygen partial pressures, as in air.^{4,5} The newly formed SiO₂ will then react again as outlined in the above and the SiC will be consumed in the continuing hot-corrosion/reoxidation process.

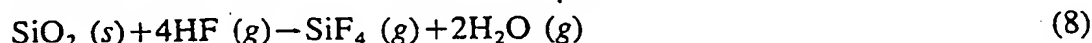
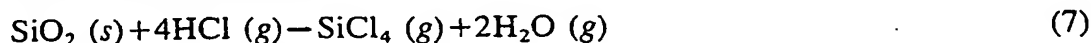
A secondary reaction can be expected to aggravate the degradation by condensing fluxes and surface glazes. Under conditions of low oxygen partial pressures ($\approx \text{PO}_2 < 3 \times 10^{-4}$ atm) "active" oxidation of SiC becomes the predominant mode of oxide formation.^{4,5}



The halide constituents of the stack gases can be expected to react with the protective SiO₂ layer on the heat transfer surfaces. Small but consistent quantities of HCl and HF have been detected in both gas phase (0.38–0.40 ppm HCl; 0.04–0.08 ppm HF) and condensate (145–552 ppm HCl, 5–14 ppm HF).⁵ Presumably, these species were formed in reactions, such as



Attack on the SiO₂ surface layer by hydrogen halides could result in the formation of volatile silicon halides.⁵



Because of the low HCl and HF concentrations and the preponderance of alkali constituents in the surface glaze (Table I), the latter reactions should be considered secondary to the principal salt-fluxing and glaze-fluxing mechanisms.

The corrosion reactions lead to rapid degradation of the silicon carbide tube surfaces, and wall recession rates in the range of 0.25–1.00 cm (100–400 mil) on an annual basis have been observed in aluminum remelt operations using fluorine-containing fluxes.

Figure 5 shows the reduction in wall thickness of a SiC tube exposed for 4200 hours in a fluorine-containing aluminum remelt environment. A new tube is shown for comparison. In the heat exchanger wall, thinning was observed to be particularly severe for the rows of tubes in the module that are contacted first by the exhaust gas stream. Tube recession is increased for the side of the tube facing the exhaust gas stream. The differential thinning of the exposed tube in Fig. 5 is noticeable in this respect.

Figure 6 shows tube wall recession rates as a function of temperature for α -sintered SiC (Hexoloy®/Sohio) and reaction-bonded SiC (SCR 210, Coors) tubes. The data were obtained by estimating temperatures over the length of a heat exchanger tube using a finite element model (ANSYS). The results of the analytically determined temperature map were integrated with wall recession data of tubes exposed for 4200 hours in an aluminum remelt environment using a fluorine-based flux. These data were then averaged to obtain a ceramic tube lifetime vs maximum material temperature.¹ It can be seen that tube life is reduced to about one year in a severely corrosive environment at 871 °C (1600 °F) (Fig. 7).

Coating Development

Materials testing indicated the ceramic recuperators⁵ using silicon carbide tubular components could not achieve their full energy savings potential in severely corrosive environments such as found in aluminum remelters using fluorine-containing base fluxes. A program was, therefore, initiated with the support of the Gas Research Institute (GRI Contract No. 5086–232–1233) to develop a protective coatings technology for silicon-based materials used as heat transfer surfaces for ceramic recuperators operating in corrosive environments.

The function of the protective coatings is twofold. First, they create a barrier between the silicon carbide tube surface and the condensing corrosive species in the stack gases. The process of active oxidation which degrades the normally protective SiO₂ layer is reduced. Second, certain refractory oxides present in the coating

will combine with the corrosive species to "freeze-up" the glazes at the tube surface. The increased viscosity of these surface glazes lessens hot corrosion and, hence, improves tube life.

Substrate Preparation

Conventional air plasma spraying technology was used for coating deposition. Deposition of adherent ceramic oxide coatings onto silicon carbide tubular components by conventional air plasma spraying techniques was found to require an initial surface roughening of the silicon carbide. Using mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) as the coating material because of its low coefficient of thermal expansion (5.6×10^{-6} cm/cm/°C) and α -sintered silicon carbide (Hexoloy®/Sohio) as the tubular substrate, various surface preparation techniques were investigated. Initially, an attempt was made to deposit the mullite coating onto an as-received α -sintered silicon carbide tube section, cleaned with methyl ethyl ketone (MEK). The mullite coating had essentially no adherence to the as-received tube section. A second tube section was grit blasted with 20-grit silicon carbide particles and cleaned with MEK prior to coating application. This grit blasting method improved the coating adherence somewhat, but not to an appreciable degree. Using a proprietary surface preparation technique, a third tube section was prepared and coated with mullite. This method of surface preparation allowed a uniform, adherent 5 mil mullite coating to be deposited onto the α -silicon carbide tube section.

The mullite coated tube section was subjected to two thermal treatments to further test the coating adherence. The coated tube section was initially isothermally heat treated at 1093 °C (2000 °F) for 120 hours. Following this heat treatment the coating retained its adherence, showing no cracks or spalling. The coated tube section was also exposed to a cyclic heat treatment consisting of 60 hourly shocks from 1010–371 °C (1850–700 °F). The mullite coating again showed excellent adherence with no cracking or spalling.

Coating Application

Using the proprietary surface preparation technique, a series of commercially available ceramic oxide plasma spray powders were deposited onto α -sintered silicon carbide (Hexoloy®/Sohio) tube sections. Coating materials investigated included mullite, zircon, spinel, chromia, alumina, yttria, zirconia, calcia-stabilized zirconia, yttria-stabilized zirconia, and calcium titanate. Each of these materials was deposited as a 20-mil-thick coating onto the prepared tube sections. All of the coatings showed excellent as-coated adherence (Fig. 8). Following an isothermal heat treatment at 1093 °C (2000 °F) for 120 hours, a 20 mil mullite coating was the only coating with no cracking or spalling. The chromia, spinel, and zirconia coatings had tensile cracks and easily flaked off the substrate. The alumina coating had tensile cracks but retained its adherence. The higher expansion materials, yttria, yttria-stabilized zirconia, calcia-stabilized zirconia, and calcium titanate completely spalled off due to their expansion mismatch with the substrates. The 20-mil-thick mullite coating was also exposed to a cyclic thermal treatment. The coating withstood 60 hourly shocks from 1010–371 °C (1850–700 °F) without cracking or spalling.

A micrograph of the silicon carbide/mullite (20 mils) coating interface following both thermal treatments is given in Fig. 9. The coating had excellent adherence to the substrate with no tensile cracking. Subsequently, mullite coatings as thick as 50 mils have been deposited. The latter coatings withstood both the isothermal and cyclic thermal screening without cracking or spalling.

A thinner (5-mil) coating of yttria-stabilized zirconia was deposited onto an

α -sintered silicon carbide (Hexoloy®/Sohio) tube section and exposed to both thermal treatments. The 5-mil yttria-stabilized zirconia coating showed excellent adherence and no visually observable cracks. However, after microscopic evaluation, tensile cracking could be seen throughout the coating (Fig. 10), presumably because of the expansion mismatch between the coating and the substrate.

Substrate Testing

The two ceramic oxide materials selected for application to various silicon carbide substrate materials were mullite and zircon. Both have low coefficients of thermal expansion (5.6×10^{-6} cm/cm/°C), close to the theoretical coefficient of thermal expansion of silicon carbide (4.7×10^{-6} cm/cm/°C). A 20-mil mullite coating and a 15-mil zircon coating were deposited onto α -SiC (Hexoloy®/Sohio), SCRB-210 (Coors), NC-430 (Norton) and CS-101K (Norton) tube sections. Table II gives the adherence results of both coatings on each substrate material following the isothermal and cyclic thermal treatments. As seen in the table, the mullite coating was compatible with all four substrate materials, showing no cracking or spalling after the thermal treatments. The zircon coating was compatible with the SCRB-210, CS-101K, and NC-430 (minimal flaking at edges), but completely spalled off the α -SiC tube section.

Advanced Coating Systems

In order to utilize the higher expansion oxide materials such as alumina and yttria-stabilized zirconia, more advanced coating systems were developed. Initially a graded or layered approach was investigated. The following coating system was deposited onto an α -sintered silicon carbide (Hexoloy®/Sohio) tube section.

Coating layer	Coefficient of thermal expansion (cm/cm/°C)
Mullite	5.6
Alumina	8.0

Since mullite is adherent to the α -sintered silicon carbide, it was used as a bond coat for the higher expansion alumina to help bridge the expansion mismatch between the alumina and the silicon carbide substrate. This coating withstood the isothermal and cyclic thermal treatments with no observable cracking or spalling. However, on further microscopic evaluation, tensile cracking was observed within the coating (Fig. 11).

To further reduce the stresses due to the thermal expansion mismatch, a more gradual change in the thermal expansion from mullite to alumina was examined. The following coating system was deposited onto a α -sintered silicon carbide tube section and exposed to both thermal treatments.

Coating material (Volume %)	Coefficient of thermal expansion (cm/cm/°C)
Mullite	5.6
75% Mullite/25% alumina	6.4
50% Mullite/50% alumina	7.2
25% Mullite/75% alumina	8.0
Alumina	8.8

This coating configuration survived both thermal treatments with no observable cracking or spalling. On further microscopic evaluation, no tensile cracking was observed for the coating and the coating/substrate interface showed excellent adherence (Fig. 12).

Using this gradual change of expansion by mixing various oxide materials, even more complex coating systems can be successfully deposited such as coating blends from mullite to alumina to yttria-stabilized zirconia. This coating technique allows ceramic oxides with higher coefficients of thermal expansion and greater chemical stability to be utilized in corrosion resistant coatings for severely aggressive environments.

Seal Coat

Because of the inherent porosity of plasma sprayed oxide coatings, a sealing mechanism for the outer coating surface may be required to prevent infiltration of corrosive species into the coating. To prevent this infiltration, a 3-mil layer of a Solaramic vitreous phase ceramic seal coating was slurry sprayed and fired onto the outer surface of a 20-mil mullite coating. This coating system was subjected to the standard isothermal and cyclic heat treatment to examine the compatibility of the vitreous phase ceramic seal coat with the plasma sprayed mullite coating. The coating system withstood both thermal treatments with no cracking or spalling.

Coating Configurations for Environmental Exposure Testing

Table III contains 10 coating systems that were developed for testing in an aluminum reclamation simulator. These 10 coatings were deposited as 3-inch bands onto 5 α -sintered silicon carbide (Hexoloy[®]/Sohio) and 5 SCRB-210 reaction-bonded silicon carbide (Coors) heat exchanger tubes. Figure 13 shows the coated tubes in front of the aluminum remelt simulator. The simulator was designed to test a two by five matrix of tubes which allows two tubular substrate materials to be tested simultaneously at five temperature ranges. Rig testing is scheduled to commence early in 1988.

Summary

A ceramic recuperator utilizing silicon carbide (SiC) tubular components has successfully operated for over 13 000 hours in an aluminum remelt furnace. Maximum gas side inlet temperature was 1010 °C and maximum air preheat was 600 °C. Overall thermal effectiveness was 55%. Tube life is substantially reduced in a severely corrosive aluminum remelt environment using fluorine-containing fluxes. Corrosion attack proceeds via fluxing of the SiO₂ surface layer on the SiC tubular components to give reactive surface glazes. Alkali and halide species in the gas phase are believed to be involved in tube corrosion.

Protective coatings technology was developed to create a barrier between the SiC tube surface and the condensing corrosive species in the stack gases. Certain refractory oxides in the coating can be expected to combine with the corrosive species to freeze-up the surface glazes.

Adherent ceramic oxide coatings (up to 50 mils thick) were deposited onto various silicon carbide heat exchanger tube materials using air-plasma spray technology. Of the single oxide coatings, mullite was observed to be superior in terms of adherence and microstructural integrity on a number of silicon carbide substrates. Single- and multi-layered (graded- α) coatings of mullite, zircon, alumina,

yttria, and yttria-stabilized zirconia remained adherent and crack free after isothermal heat treatment at 1093 °C (2000 °F)/120 hours followed by cyclic heat treatment (60 one-hour cycles) between 1010° and 371 °C (1850° and 700 °F).

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Table I. Typical Composition of Surface Corrosion Deposits (% by Weight)

Material	Deposition
Si	31-46%
Na	4-12%
K	4-10%
Al	1-3%
Fe	0.1-5%
C	2-5%
F	33-100 ppm
O	balance

Table II. Compatibility of Mullite and Zircon with Various Silicon-Based Ceramics

Substrate	Vendor	Zircon (15 mils)			Mullite (20 mils)		
		As-sprayed	Isothermal	Cyclic	As-sprayed	Isothermal	Cyclic
α -SiC	Sohio	Good	Severe spalling	Severe spalling	Good	Good	Good
NC-430	Norton	Good	Flaked off at edges	No further flaking	Good	Good	Good
CS-101K	Norton	Good	Good	Good	Good	Good	Good
SCRB-210	Coors	Good	Good	Good	Good	Good	Good

Table III. Coatings for Environmental Exposure Tests

Coating No.	Materials	Thickness (mil)
1	Mullite+glass seal coat	20
2	Mullite	20
3	Mullite	30
4	Mullite	10
	75 Mullite/25 Al_2O_3	5
	50 Mullite/50 Al_2O_3	5
	25 Mullite/75 Al_2O_3	5
	Al_2O_3	5
5	Mullite	10
	75 Mullite/25 Al_2O_3	5
	50 Mullite/50 Al_2O_3	5
	25 Mullite/75 Al_2O_3	5
	Al_2O_3	5
	75 Al_2O_3 /25 ZrO_2 (8) Y_2O_3	3
	50 Al_2O_3 /50 ZrO_2 (8) Y_2O_3	3
	25 Al_2O_3 /75 ZrO_2 (8) Y_2O_3	3
	ZrO_2 (8) Y_2O_3	3
6	50 Mullite-50 Zircon	20
7	Mullite-Zircon	10
	75 Mullite-Zircon/25 Al_2O_3	5
	50 Mullite-Zircon/50 Al_2O_3	5
	25 Mullite-Zircon/75 Al_2O_3	5
	Al_2O_3	5
8	Mullite-Zircon	10
	75 Mullite-Zircon/25 Al_2O_3	5
	50 Mullite-Zircon/50 Al_2O_3	5
	25 Mullite-Zircon/75 Al_2O_3	5
	Al_2O_3	5
	75 Al_2O_3 /25 ZrO_2 (8) Y_2O_3	3
	50 Al_2O_3 /50 ZrO_2 (8) Y_2O_3	3
	25 Al_2O_3 /75 ZrO_2 (8) Y_2O_3	3
	ZrO_2 (8) Y_2O_3	3
9	Mullite	10
	75 Mullite/25 Y_2O_3	5
	50 Mullite/50 Y_2O_3	5
	25 Mullite/75 Y_2O_3	5
	Y_2O_3	5
10	Mullite	10
	80 Mullite/20 ZrO_2 (8) Y_2O_3	5
	60 Mullite/40 ZrO_2 (8) Y_2O_3	5
	40 Mullite/60 ZrO_2 (8) Y_2O_3	5
	20 Mullite/80 ZrO_2 (8) Y_2O_3	5
	ZrO_2 (8) Y_2O_3	5

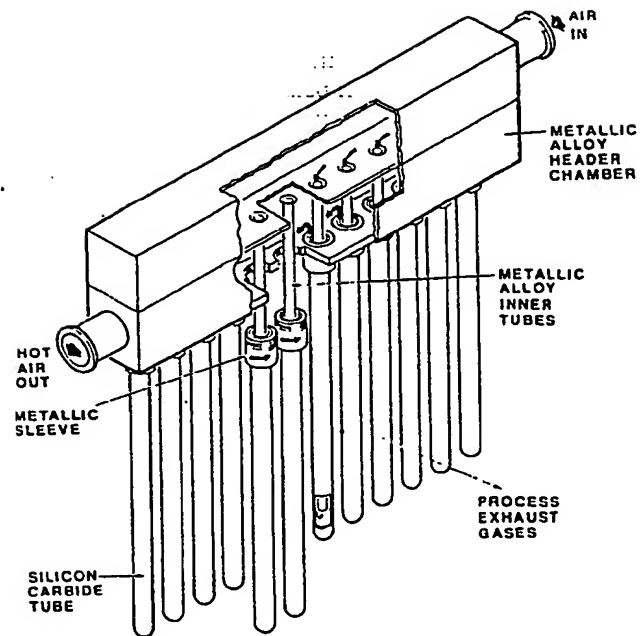


Fig. 1. Schematic of self-contained recuperator module.

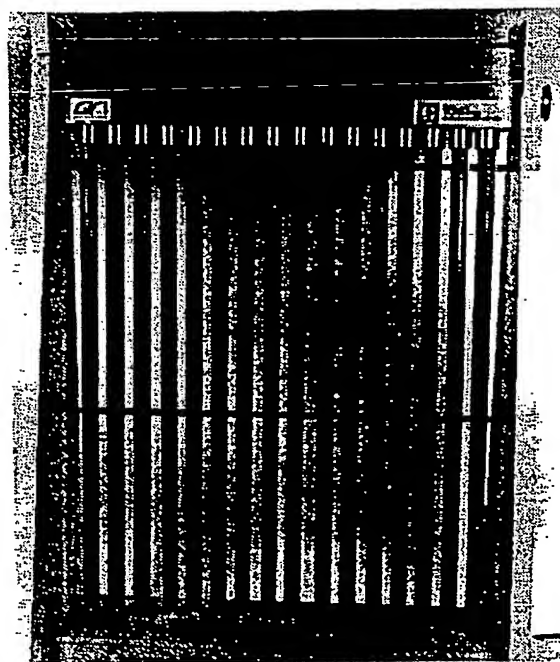


Fig. 2. Self-contained recuperator module.

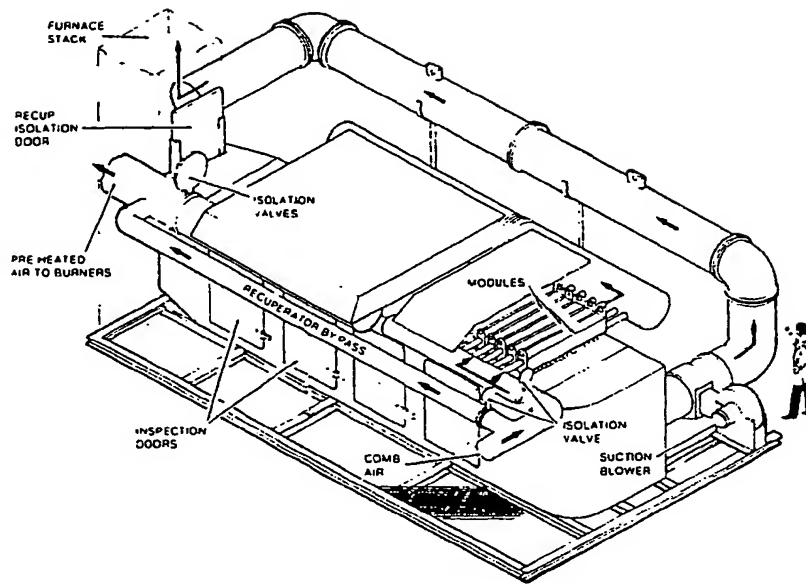


Fig. 3. Schematic of a two-pass recuperator.

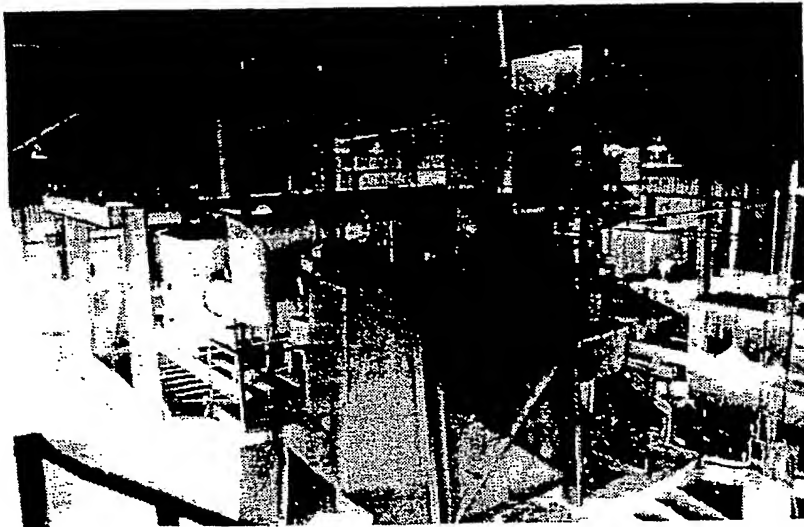


Fig. 4. Recuperator in operation at TIMCO Inc., Fontana, CA.

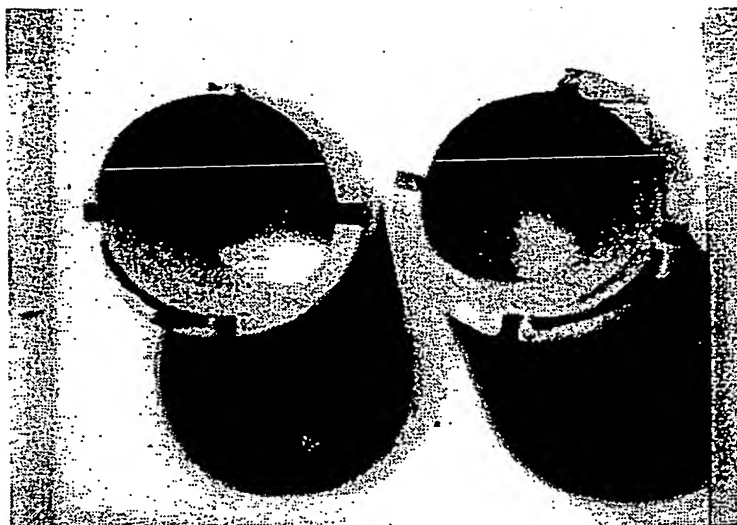


Fig. 5. Tube sections. Right—new tube; left—tube exposed for 4200 hours in fluorine-containing aluminum remelt environment. Notice differential wall thinning.

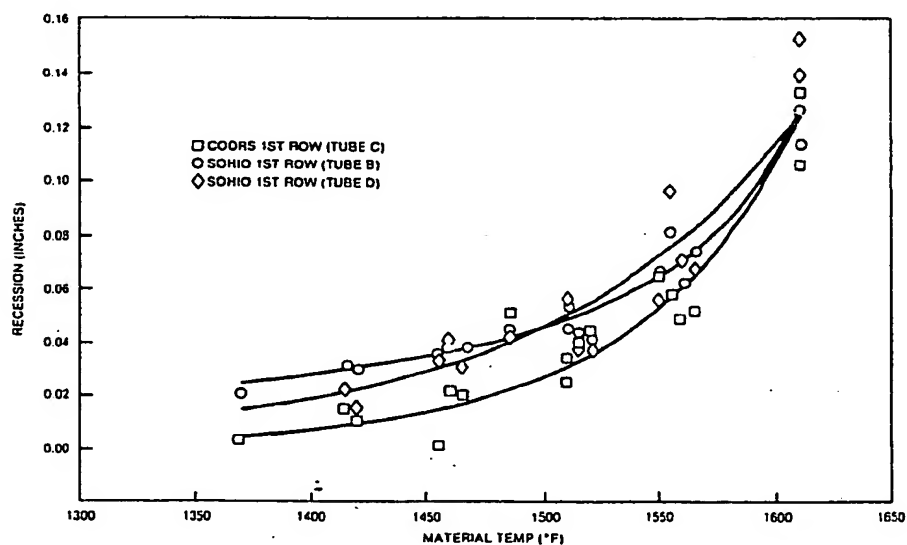


Fig. 6. Wall recession rates as a function of temperature for Hexoloy (Sohio) and SCRB-210 (Coors) tubes.

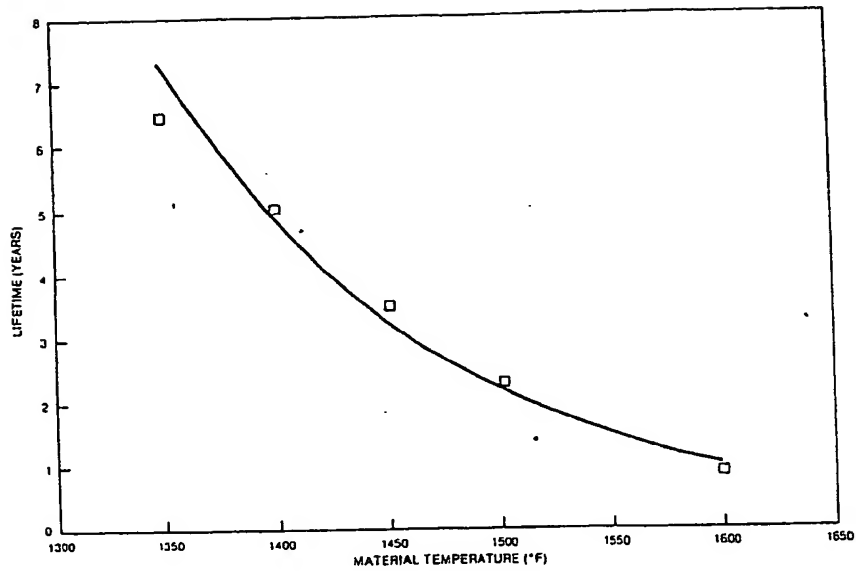


Fig. 7. Tube lifeline vs material temperature.

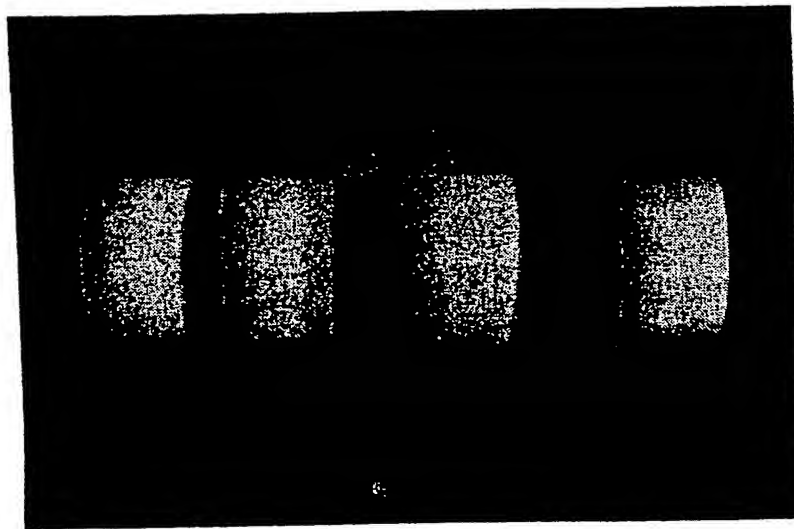


Fig. 8. α -SiC tube coated with ceramic oxide materials. Coatings: (left to right) Mullite, Y_2O_3 -stabilized ZrO_2 , CaO-stabilized ZrO_2 , ZrO_2 . Coating thickness: approximately 20 mils.

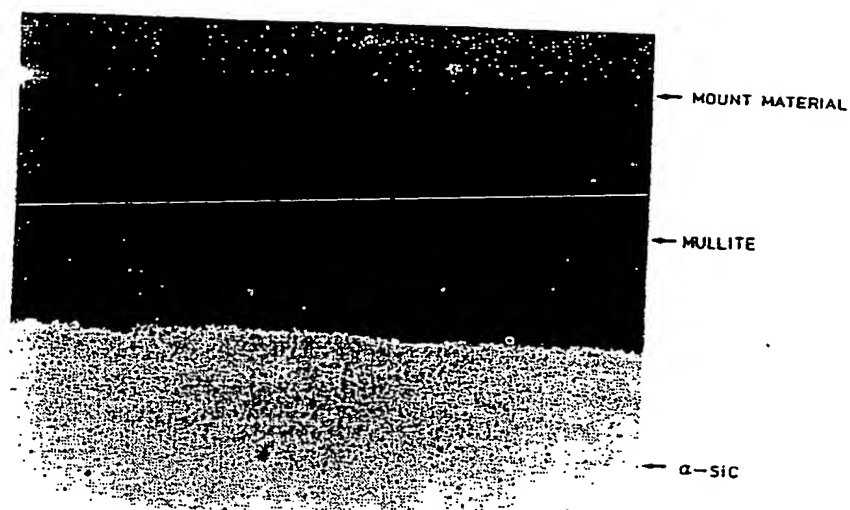


Fig. 9. Coating/substrate interface for mullite coated α -SiC after isothermal ($1093^{\circ}\text{C}/120$ hrs) and cyclic (1010° - $371^{\circ}\text{C}/60$ one-hour cycles) heat treatments.

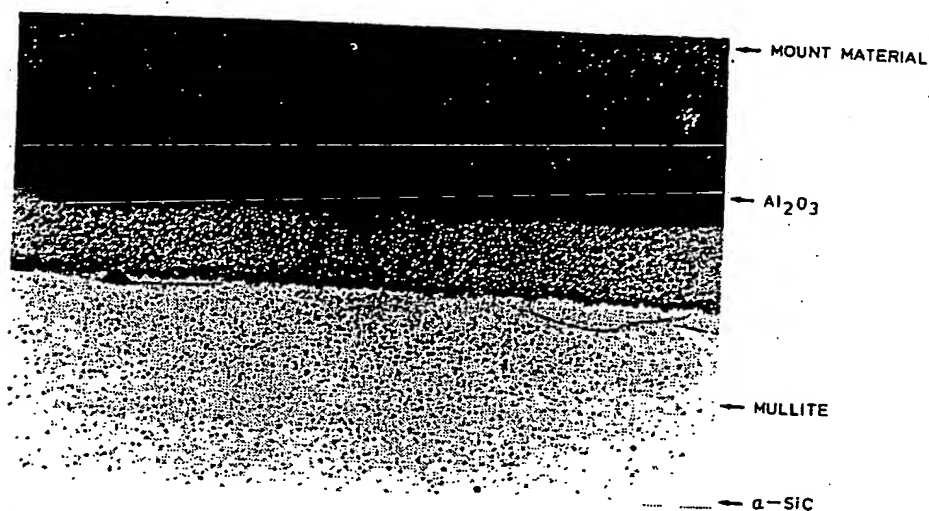


Fig. 10. Coating/substrate interface for Y_2O_3 -stabilized ZrO_2 coated α -SiC after isothermal ($1093^{\circ}\text{C}/120$ hrs) and cyclic (1010° - $371^{\circ}\text{C}/60$ one-hour cycles) heat treatments.

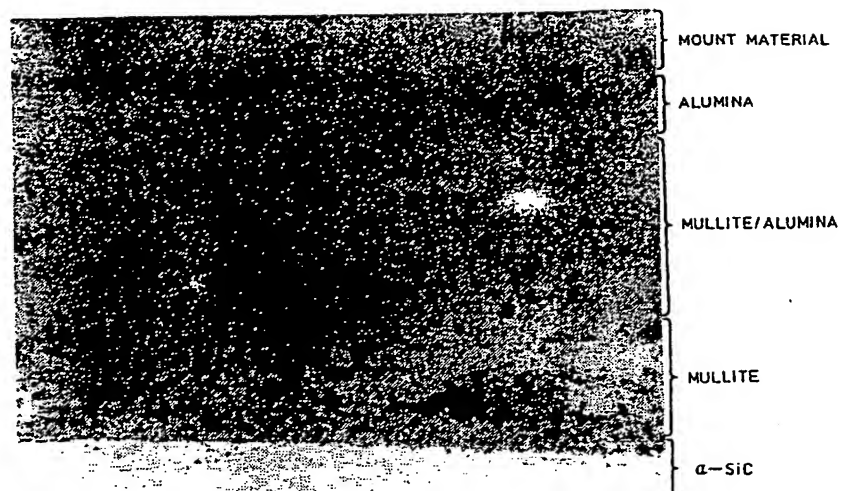


Fig. 11. Coating/substrate interface of layered- α coating of mullite and alumina on α -SiC after isothermal ($1093^{\circ}\text{C}/120$ hours) and cyclic ($1010^{\circ}\text{--}371^{\circ}\text{C}/60$ one-hour cycles) heat treatment.

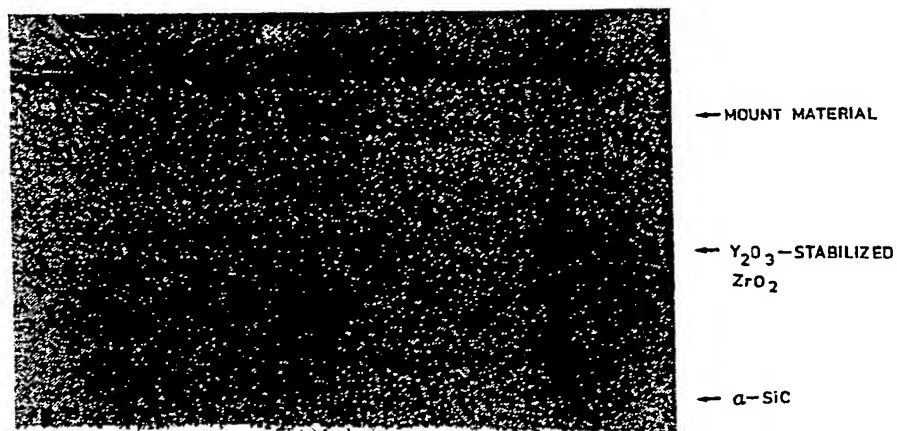


Fig. 12. Interface of the gradually mixed- α coating of mullite and alumina on α -SiC after isothermal ($1093^{\circ}\text{C}/120$ hours) and cyclic ($1010^{\circ}\text{--}371^{\circ}\text{C}/60$ one-hour cycles) heat treatment.

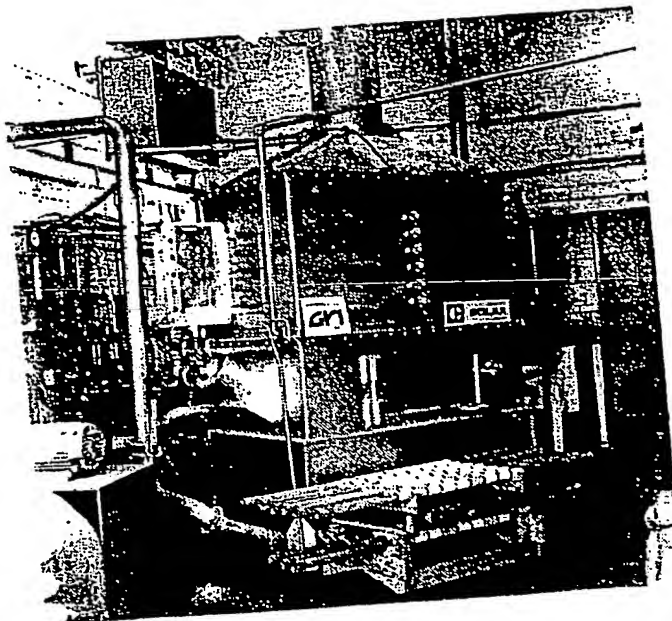


Fig. 13. Aluminum remelt simulator and coated tubular materials.

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